ONTARIO MINISTRY OF ENVIRONMENT
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INTERLABORATORY STUDY 96-1

TOTAL ALKALINITY, CATIONS, ANIONS AND TRACE METALS IN WATER

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Report Prepared by

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Project QMU96-01

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INTERLABORATORY STUDY 96-1

1 INTRODUCTION

In January and early February of 1996, a major survey of lakes in the Sudbury Ontario area was jointly undertaken by the Ontario Ministry of the Environment and Energy (MOEE) and Laurentian University. Additional sampling was also carried out before the ice melted at the beginning of April 1996. The Quality Management Unit (QMU) of the MOEE Laboratory Services Branch (LSB) was asked to provide a set of check samples to be split between the three laboratories that would be analyzing the samples. The participating laboratories were LSB in Toronto (two analytical sections: Water Quality Analysis (WQA) and Client Services, Metals & Microbiology (CSMM)), the MOEE Regional laboratory in Thunder Bay (TB), and the Central Process Laboratory of INCO Ltd. in Sudbury (INCO). Two sets of samples were prepared and distributed, one at the end of January 1996, and a second set at the beginning of April 1996. Target parameters were Total Fixed Endpoint Alkalinity (subsequently referred to as Alkalinity), Calcium, Magnesium, Sodium, Potassium (Cations), Chloride, Sulphate (Anions), and four Trace Metals (Aluminum, Copper, Nickel and Zinc).

2 SAMPLE PREPARATION AND DISTRIBUTION

All samples were prepared using deionized reverse osmosis (RO) water. All spiking solutions were from ampouled stock solutions routinely used by the QMU for their Performance Evaluation Program (PEP). Spiking levels were also taken from levels routinely used as part of the PEP procedures. All samples were prepared using volumetric glassware and transferred to PET bottles. Samples for Trace Metals were preserved with 2% Nitric Acid.

The first set of samples was prepared on January 30, 1996. Samples for INCO and TB were shipped by courier the same afternoon for next day delivery. Samples for LSB were hand delivered.

Results were reported by the WQA section for Alkalinity, Anions and Cations on February 15, 1996. Concern was expressed, as only Sodium was found in the Cation samples and nothing was detected in the Anion samples. Telephone conversations with TB and INCO confirmed this finding. Upon investigation, it was discovered that the Cation solutions had been transferred into the PET bottles pre-labelled for the Anion samples, and the Anion solutions had been transferred into the PET bottles pre-labelled for the Cation samples. A second set of Cation and Anion solutions was prepared on February 21, 1996, and the sample number codes had the suffix "A". Samples for INCO and TB were shipped by courier the same afternoon for next day delivery. Samples for LSB were hand delivered. All results for the first set of samples were received by May 30, 1996.

The second set of samples was prepared on April 9, 1996, using the same spiking levels as the first set. Samples for INCO and TB were shipped by courier the same afternoon for next day delivery. Samples for LSB were hand delivered. All results for the second set were received by June 21, 1996.

3 DISCUSSION

All results are listed in Table 1 of Appendix 1. The mean, median, and standard deviation are calculated for each parameter. The percent difference from the target was calculated for each result and is listed in Table 2. A list of the methodology is given in Table 3.

Each sample set included a High Spike and a Low Spike. These results are paired and plotted on a graph using the Youden[1] technique. Results from both sets of samples are included on

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the same graph. The graphs are divided into quadrants by lines drawn through the intersection of the target values. An area of acceptable performance (see below) is centred around the target values. Results in the upper right quadrant outside the acceptance criteria are considered biased high, while results in the lower left quadrant outside the acceptance criteria are considered biased low. Results in the upper left or lower right quadrants outside the acceptance criteria are considered erratic. A line is drawn from the origin through the target value as a means of assessing within-laboratory precision. As the scales of the individual graphs may not always include the origin, the lines appear to vary in their location, but all have been drawn to pass through (0,0).

The MOEE/Laurentian University lake survey project did not have established performance criteria prior to this intercomparison. As three results are not enough data points to calculate performance criteria from a statistical perspective, performance criteria was adopted from that used by the National Water Research Institute (NWRI) of Environment Canada[2,3]. This performance criteria has been used for both the Long-Range Transport of Acidic Precipitation (LRTAP) interlaboratory studies and the current Ecosystem Interlaboratory QA Program. An explanation of the derivation of the performance criteria is given in Appendix 3. The area of acceptable performance appears on each graph, centred on the target values. The areas appear as ellipses, due to the difference in scale of the two samples.

The scales of the graphs were adjusted to make it possible to identify the individual data points. This should be considered when looking at the graphs, as the spread between the laboratories may appear greater than would be considered significant. All graphs are in Appendix 2.

3.1 Alkalinity

The Total Fixed Endpoint Alkalinity test is defined as having an endpoint of pH 4.5 for the titration. As distilled water has a pH of 7.0, by the definition of the test, distilled water has a small amount of "Alkalinity". The value reported by each laboratory for the unspiked sample (ALK96-1-01) was subtracted from the values reported for the spiked samples (ALK96-1-02 and ALK96-1-03). The "corrected" values were used to prepare the Youden plot (Figure 11).

All three laboratories demonstrated good agreement with the target and with each for the first set of samples (Table 2 and Figure 11). All three laboratories had good within-laboratory precision, as the results for the January samples are close to the diagonal line (Figure 11).

LSB (WQA) maintained good performance for the second set of samples, with results close to the target and good within-laboratory precision. INCO maintained their within-laboratory precision, but were biased high (upper right quadrant and outside NWRI performance limits) for the second set of samples. This suggests that there may have been a change in standards between the two sets of samples and should be investigated. TB demonstrated poorer performance for the second set of samples, as they were biased low (lower left quadrant and on the edge of the NWRI performance criteria) and less precise (Figure 11).

3.2 Calcium, Magnesium, Sodium and Potassium (Cations)

All three laboratories demonstrated good within-laboratory precision for both sets of samples, as all data points are close to the diagonal line (Figure 5). LSB and TB demonstrated consistent performance for both sets of samples, though TB is high (6-7% from target and outside the NWRI performance limits). The INCO lab had results just at the lower limit for the first set of samples, but were biased high (>10% of target and

outside the NWRI performance limits; Figure 5) for the second set of samples. This suggests that there may have been a change in the calibration standards or in the method between the two sample sets and should be investigated.

All three laboratories demonstrated good within-laboratory precision for Magnesium for both sets of samples (Figure 6). LSB (WQA) had good agreement with the target values. The TB laboratory's results shifted high for the second set of samples. The INCO laboratory is biased high (>10% of target and outside NWRI performance limits).

LSB (WQA) demonstrated good agreement with the target and within-laboratory precision for Sodium for both sets of samples. The INCO laboratory improved their performance in the second set of samples compared to the first set (Table 2). The TB laboratory was biased high and outside the NWRI performance limits for both sample sets (Figure 7).

The TB laboratory reported a positive value in the unspiked sample (CAT96-01A) for Potassium. This was subtracted from the results reported for CAT96-1-02A and CAT96-1-03A for the values used for the Youden plot (Table 1 and Figure 8). Both LSB (WQA) and TB had good agreement with the target and within-laboratory precision for the first set of samples. Their performance was less precise and slightly high for the second set of samples (on edge of NWRI performance limits; Figure 8). The INCO laboratory was outside the NWRI performance limits for the first set of samples and improved their performance for Potassium in the second set of samples.

3.3 Chloride and Sulphate (Anions)

LSB (WQA) and TB demonstrated good within-laboratory precision and agreement with the target value for Chloride for both sets of samples (Figure 9). The INCO laboratory had Chloride results below the target for the first set of samples (AN96-1-02A was -10%), but were shifted high (+6% for the low spike and +12% for the high spike; Table 2) for the second set of samples. This suggests that there may have been a change in the calibration standards or in the method between the two sample sets and should be investigated.

The TB and INCO labs agreed with each other for Sulphate in both sets of samples (Figure 10). Both laboratories had good agreement with the target for the high spikes. For the first set of low spikes they were slightly below the target and for the second set they were slightly higher than the target. LSB (WQA) had good agreement with the target values for Sulphate for the first set of samples, though they were slightly higher than the other two laboratories. For the second set of samples, LSB (WQA) was high relative to the other laboratories and to the target, and also outside the NWRI performance criteria. This suggests that there may have been a change in the calibration standards or in the method between the two sample sets and should be investigated.

3.4 Trace Metals (Aluminum, Copper, Nickel and Zinc)

The results for Aluminum demonstrate variable performance by all three laboratories for both sets of samples (Figure 1). For the first set of samples, all three laboratories were high relative to the target for the low spike (MET96-01-2), and outside the NWRI performance limits. However, for the high spike (MET96-01-3), while all three laboratories were high relative to the target, they all fall within the NWRI performance criteria. This suggests an intercept problem for all of the laboratories. For the second set of samples, the INCO and TB laboratories have closer agreement with the target and are within the NWRI performance criteria (Figure 1). LSB (CSMM)'s results for the second set of samples continue to show a high bias and are outside the NWRI performance criteria for

both samples. Previous use of the spiking solution for the QMU PE Program does not indicate a problem with the target values[4]. Contamination from the nitric acid can be ruled out, since such a contamination should have affected all samples equally, including the unspiked samples. Such was not the case. Even though all glassware used in the preparation of the samples was meticulously acid washed and cleaned, contamination during sample preparation cannot be ruled out. However, given the variability that has been previously seen with Aluminum data, both within the LSB PE Program as well as the NWRI interlaboratory studies, it is extremely unusual that three laboratories would independently report the same value.

The TB laboratory had good agreement with the target for Copper in the first set of samples. The INCO laboratory was high for Copper in the low spike (MET96-01-2), but the high spike was just within the upper NWRI performance limit in the first sample set. LSB (CSMM) was biased high (6-10%) and outside the NWRI performance limits. TB and LSB (CSMM) shifted up by approximately 10% in the second set of samples, though TB stayed within the NWRI performance limits. The INCO lab shifted down by approximately 7% and moved within the NWRI performance limits.

The TB laboratory demonstrated consistent performance for both sets of samples for Nickel. The INCO laboratory improved its performance for Nickel in the second set of samples compared to the first set of samples. LSB (CSMM) may have developed a slope problem in their calibration curve between the two sets of samples, as the difference from the target increased by 6% for the high spike, but decreased slightly (-1.5%) for the low spike. However all results from all laboratories were within the NWRI performance limits (Figure 3).

The INCO and TB laboratories demonstrated an improvement in performance for Zinc in the second set of samples compared to the first set of samples. Both laboratories had identical results for both sets of samples (Table 1 and Figure 4). LSB (CSMM) demonstrated good within-laboratory precision for both sets of samples, but they shifted higher from the target, from 6% to 11%, in the second set of samples. However all results from all laboratories were within the NWRI performance limits.

The spiking solution used to prepare the Trace Metal solutions also contained additional parameters to those requested for the study. Participants were given the option of reporting additional results. Only the INCO laboratory reported additional results for the second set of samples and these are given in Table 4. Two parameters may have intercept problems, Iron and Lead, as the INCO laboratory was biased high (>10%) for the low spike (MET96-01-5). All other results demonstrated good agreement with the target.

4 CONCLUSION

Between-laboratory performance was generally consistent for Alkalinity, Cations and Anions. Data points were considered biased if they exceeded the NWRI performance criteria and it was noted if they differed from the target by more than 10% No results for this group of parameters differed from the target by more than 15%.

Performance for the Trace Metals was more variable. Each participant had a change in the quality of performance for different metals between the two sets of samples. There may be an intercept problem for Aluminum. No clear pattern was evidenced for the other three metals. Frequent validation of calibration standards using Standard Reference Materials may help to reduce the interlaboratory variability.

Overall, all three laboratories demonstrated good within-laboratory precision. LSB had fewer data points outside the NWRI performance limits than the other two laboratories. The three laboratories agreed within 10% of each other for all parameters in all samples, except for Alkalinity in ALK96-1-05 (CV = 12.3%).

5 REFERENCES

5.1 Youden, W.J. and Steiner, E.H.; 1975. *Statistical Manual of the Association of Official Analytical Chemists*. Association of Official Analytical Chemists; ISBN 0-935584-14-3.

5.2 Aspilla, Keijo, et al; 1983-1996. *LRTAP Interlaboratory Studies L-01 to L39 for Major Ions and Nutrients*. National Water Research Institute, Burlington, Ontario.

5.3 Alkema, H., et al; 1993-1996. *Ecosystem Interlaboratory QA Program Studies FP062 - FP068, Major Ions & Nutrients and Total Phosphorus in Surface Waters and Trace Metals in Surface Waters*. National Water Research Institute, Burlington, Ontario.

5.4 Selliah, S.S.; July 5, 1996. LSB PEP results. Personal communication.

6 APPENDIX 1 - TABLES OF RESULTS

TABLE 1

INTERLABORATORY STUDY 96-1

PART 1, JANUARY 1996

SAMPLE	TARGET	LSB	TB	INCO	MEAN	SD	CV	MEDIAN
ALKALINITY mg/L								
ALK96-1-01	-	1.51	1.6	2.5	1.87	0.55	29.4%	1.6
ALK96-1-02	14	15.7	16.0	16.1	15.93	0.21	1.3%	16.0
ALK96-1-03	30	31.9	32.0	33.3	32.40	0.78	2.4%	32.0
CORRECTED FOR BLANK								
ALK96-1-02	14	14.19	14.4	13.6	14.06	0.41	2.9%	14.19
ALK96-1-03	30	30.39	30.4	30.8	30.53	0.23	0.7%	30.4
CALCIUM mg/L								
CAT96-1-01A	-	0.05 <W	0.05 <W	<0.1				
CAT96-1-02A	15	14.7	16.0	14.75	15.15	0.74	4.9%	14.75
CAT96-1-03A	30	29.4	32.0	28.49	29.96	1.82	6.1%	29.4
MAGNESIUM mg/L								
CAT96-1-01A	-	0.02 <W	0.02 <W	<0.1				
CAT96-1-02A	2.5	2.50	2.60	2.81	2.64	0.16	6.1%	2.60
CAT96-1-03A	5	4.99	5.30	5.48	5.26	0.25	4.7%	5.30
SODIUM mg/L								
CAT96-1-01A	-	0.02 <W	0.05 <W	<0.1				
CAT96-1-02A	12.5	12.5	13.0	13.21	12.90	0.36	2.9%	13.0
CAT96-1-03A	25	25.5	27.0	25.92	26.14	0.77	2.9%	25.92
POTASSIUM mg/L								
CAT96-1-01A	-	0.01 <W	0.05 <T	<0.1				
CAT96-1-02A	2.5	2.51	2.6	2.77	2.63	0.13	4.9%	2.5
CAT96-1-03A	5	5.01	5.1	5.12	5.08	0.06	1.2%	5.1
CORRECT TB FOR BLANK								
CAT96-1-02A	2.5	2.51	2.55	2.77	2.61	0.14	5.3%	2.55
CAT96-1-03A	5	5.01	5.05	5.12	5.06	0.06	1.2%	5.05
CHLORIDE mg/L								
AN96-1-01A	-	0.2<W	0.05 <W	<2				
AN96-1-02A	5	4.9	5.14	4.5	4.85	0.32	6.6%	4.9
AN96-1-03A	25	24.8	25.5	23.9	24.73	0.80	3.2%	24.8
SULPHATE mg/L								
AN96-1-01A	-	0.5<W	0.5<W	<4				
AN96-1-02A	7.5	7.64	7.15	7.0	7.26	0.33	4.5%	7.15
AN96-1-03A	12.5	12.6	12.4	12.4	12.47	0.12	0.9%	12.4

PART 2, APRIL 1996

SAMPLE	TARGET	LSB	TB	INCO	MEAN	SD	CV	MEDIAN
ALKALINITY mg/L								
ALK96-1-04	-	1.68	3.4	4.7	3.26	1.51	46%	3.4
ALK96-1-05	14	15.8	15.8	20.6	17.40	2.77	16%	15.8
ALK96-1-06	30	32.4	31.8	37.8	34	3.30	9.7%	32.4
CORRECTED FOR BLANK								
ALK96-1-05	14	14.12	12.4	15.9	14.14	1.75	12.3%	14.12
ALK96-1-06	30	30.72	28.4	33.1	30.74	2.35	7.5%	30.72
CALCIUM mg/L								
CAT96-1-04	-	0.05<W	0.05 <W	<1				
CAT96-1-06	15	14.6	15.8	17.2	15.90	1.30	8.1%	15.8
CAT96-1-05	30	29.5	32.3	33.7	31.83	2.14	6.7%	32.3
MAGNESIUM mg/L								
CAT96-1-04	-	0.02<W	0.02 <W	<1				
CAT96-1-05	2.5	2.52	2.80	2.6	2.71	0.16	5.9%	2.80
CAT96-1-05	5	5.10	5.58	5.7	5.46	0.32	5.8%	5.58
SODIUM mg/L								
CAT96-1-04	-	0.02<W	0.05 <W	1.8				
CAT96-1-05	12.5	12.6	14.1	12.6	13.10	0.87	6.6%	12.5
CAT96-1-06	25	26.2	28.1	25.7	26.67	1.27	4.7%	26.2
POTASSIUM mg/L								
CAT96-1-04	-	0.01<W	0.02 <W	3				
CAT96-1-05	2.5	2.61	2.7	2.6	2.64	0.06	2.3%	2.61
CAT96-1-06	5	5.08	5.1	5.2	5.13	0.06	1.2%	5.1
CHLORIDE mg/L								
AN96-1-04	-	0.2<W	0.05 <W	<2				
AN96-1-05	5	5.0	5.1	4.8	4.97	0.15	3.0%	5.0
AN96-1-06	26	25.0	26	27.0	26.00	1.00	3.8%	26
SULPHATE mg/L								
AN96-1-04	-	0.5<W	0.5 <W	<1				
AN96-1-05	7.5	8.5	7.90	8.0	8.13	0.32	3.9%	8.0
AN96-1-06	12.5	13.0	12.40	12.4	12.60	0.35	2.8%	12.40

INTERLABORATORY STUDY 96-1

PART 1, JANUARY 1996

SAMPLE	TARGET	LSB	TB	INCO	MEAN	SD	CV	MEDIAN
ALUMINUM µg/L								
MET96-01-1	-	1.63	5<W	5				
MET96-01-2	110	130	130	131	130.3	0.6	0.5%	130
MET96-01-3	264	269	290	290	283.0	12.1	4.3%	290
COPPER µg/L								
MET96-01-1	-	0.212	0.5<W	5				
MET96-01-2	17.5	19.3	17.4	20	18.90	1.35	7.1%	19.3
MET96-01-3	42	44.6	42.2	45	43.93	1.51	3.4%	44.6
NICKEL µg/L								
MET96-01-1	-	0.0906	1<W	3				
MET96-01-2	12.5	13	13	14	13.3	0.6	4.5%	13
MET96-01-3	30	31	32	32	31.7	0.6	1.9%	32
ZINC µg/L								
MET96-01-1	-	-0.03	1<W	3				
MET96-01-2	12.5	13.2	14	14	13.7	0.5	3.6%	14
MET96-01-3	30	31.8	32	32	31.9	0.1	0.3%	32

PART 2, APRIL 1996

SAMPLE	TARGET	LSB	TB	INCO	MEAN	SD	CV	MEDIAN
ALUMINUM µg/L								
MET96-01-4	-	2.24 <MDL	5<W	1.6				
MET96-01-5	110	127.64	118	123	122.9	4.8	3.9%	123
MET96-01-6	264	297.46	280	267	281.5	15.3	5.4%	280
COPPER µg/L								
MET96-01-4	-	0.82 <MDL	0.5< W	<0.1				
MET96-01-5	17.5	21.33	19.3	19	19.88	1.27	6.4%	19.3
MET96-01-6	42	47.92	43.5	42	44.47	3.08	6.9%	43.5
NICKEL µg/L								
MET96-01-4	-	0.44 <MDL	1<W	0.3				
MET96-01-5	12.5	12.81	13	13	12.9	0.1	6.9%	13
MET96-01-6	30	32.72	31	31	31.6	1.0	3.2%	31
ZINC µg/L								
MET96-01-4	-	1.39 <MDL	1<W	0.4				
MET96-01-5	12.5	14.11	13	13	13.4	0.6	4.5%	13
MET96-01-6	30	33.25	31	31	31.8	1.3	4.1%	31

CV = Coefficient of Variation

TABLE 2

INTERLABORATORY STUDY 96-1: PERCENT DIFFERENCE FROM TARGET								
PART 1, JANUARY 1996					PART 2, APRIL 1996			
SAMPLE	TARGET	LSB	TB	INCO	SAMPLE	LSB	TB	INCO
ALKALINITY (CORRECTED FOR BLANK)								
ALK96-1-02	14	1.4%	2.9%	-2.9%	ALK96-1-05	0.0%	-11.4%	13.6%
ALK96-1-03	30	1.3%	1.3%	2.7%	ALK96-1-06	2.4%	-5.3%	10.3%
CALCIUM								
CAT96-1-02A	15	-2.0%	6.7%	-1.7%	CAT96-1-05	-2.7%	8.0%	14.7%
CAT96-1-03A	30	-2.0%	6.7%	-5.0%	CAT96-1-06	-1.7%	7.7%	12.3%
MAGNESIUM								
CAT96-1-02A	2.5	0.0%	4.0%	12.4%	CAT96-1-05	0.8%	12.0%	12.0%
CAT96-1-03A	5	-0.2%	6.0%	9.6%	CAT96-1-06	2.0%	11.6%	-4.0%
SODIUM								
CAT96-1-02A	12.5	0.0%	8.0%	5.7%	CAT96-1-05	0.8%	12.8%	0.8%
CAT96-1-03A	25	0.0%	8.0%	3.7%	CAT96-1-06	4.4%	12.8%	2.8%
POTASSIUM								
CAT96-1-02A	2.5	0.4%	2.0% *	10.8%	CAT96-1-05	4.4%	8.0%	4.0%
CAT96-1-03A	5	0.2%	1.0% *	2.8%	CAT96-1-06	1.6%	2.0%	4.0%
CHLORIDE								
AN96-1-02A	5	-2.0%	2.8%	-10.0%	AN96-1-05	0.0%	2.0%	-4.0%
AN96-1-03A	25	-0.8%	2.8%	-4.4%	AN96-1-06	0.0%	8.0%	8.0%
SULPHATE								
AN96-1-02A	7.5	1.3%	-1.7%	-6.7%	AN96-1-05	13.3%	5.3%	6.7%
AN96-1-03A	12.5	0.8%	-0.8%	-0.8%	AN96-1-06	4.4%	-0.8%	-0.8%
ALUMINUM								
MET96-01-2	110	18.2%	18.2%	19.1%	MET96-01-5	16.0%	7.3%	11.8%
MET96-01-3	264	1.9%	9.8%	9.8%	MET96-01-6	12.7%	6.1%	1.1%
COPPER								
MET96-01-2	17.5	10.3%	-0.6%	14.3%	MET96-01-5	21.9%	10.3%	8.6%
MET96-01-3	42	6.2%	0.5%	7.1%	MET96-01-6	14.1%	3.6%	0.0%
NICKEL								
MET96-01-2	12.5	0.0%	8.0%	12.0%	MET96-01-5	2.5%	4.0%	4.0%
MET96-01-3	30	3.3%	6.7%	6.7%	MET96-01-6	9.1%	3.3%	3.3%
ZINC								
MET96-01-2	12.5	5.6%	12.0%	12.0%	MET96-01-5	12.9%	4.0%	4.0%
MET96-01-3	30	6.0%	6.7%	6.7%	MET96-01-6	10.8%	3.3%	3.3%

* Based on results corrected for the Blank

TABLE 3

INTERLABORATORY STUDY 96-1: METHOD/INSTRUMENTATION USED BY PARTICIPANTS			
TEST/GROUP	**LSB**	**TB**	**INCO**
Alkalinity	Auto-titration to pH 4.5	Auto-titration to pH 4.5	Titration to pH 4.5
Cations (Ca, Mg, Na, K)	AAS	AAS	ICP-MS
Anions: Chloride	Colourimetry	Colourimetry	HPLC
Anions: Sulphate	Ion Chromatography	Ion Chromatography	HPLC
Trace Metals (Al, Cu, Ni, Zn)	ICP-MS	ICP-AES	ICP-MS

TABLE 4

INTERLABORATORY STUDY 96-1: ADDITIONAL TRACE METAL RESULTS, µg/L			
PART 2, APRIL 1996			
SAMPLE	**TARGET**	**INCO**	**PERCENT DIFFERENCE FROM TARGET**
	CHROMIUM		
MET96-01-5	10	10	0.0%
MET96-01-5	24	21	0.0%
	IRON		
MET96-01-5	56	62	10.7%
MET96-01-6	134.4	140	4.2%
	COBALT		
MET96-01-5	11.5	12	0.0%
MET96-01-6	27.6	29	0.0%
	ARSENIC		
MET96-01-5	8.35	9	7.8%
MET96-01-6	20.04	21	4.2%
	CADMIUM		
MET96-01-5	7	7	0.0%
MET96-01-6	16.8	17	1.2%
	LEAD		
MET96-01-5	12.5	15	20.0%
MET96-01-6	30	32	6.7%
	SELENIUM		
MET96-01-5	10	10	0.0%
MET96-01-6	24	25	4.2%

7 APPENDIX 2 - GRAPHS

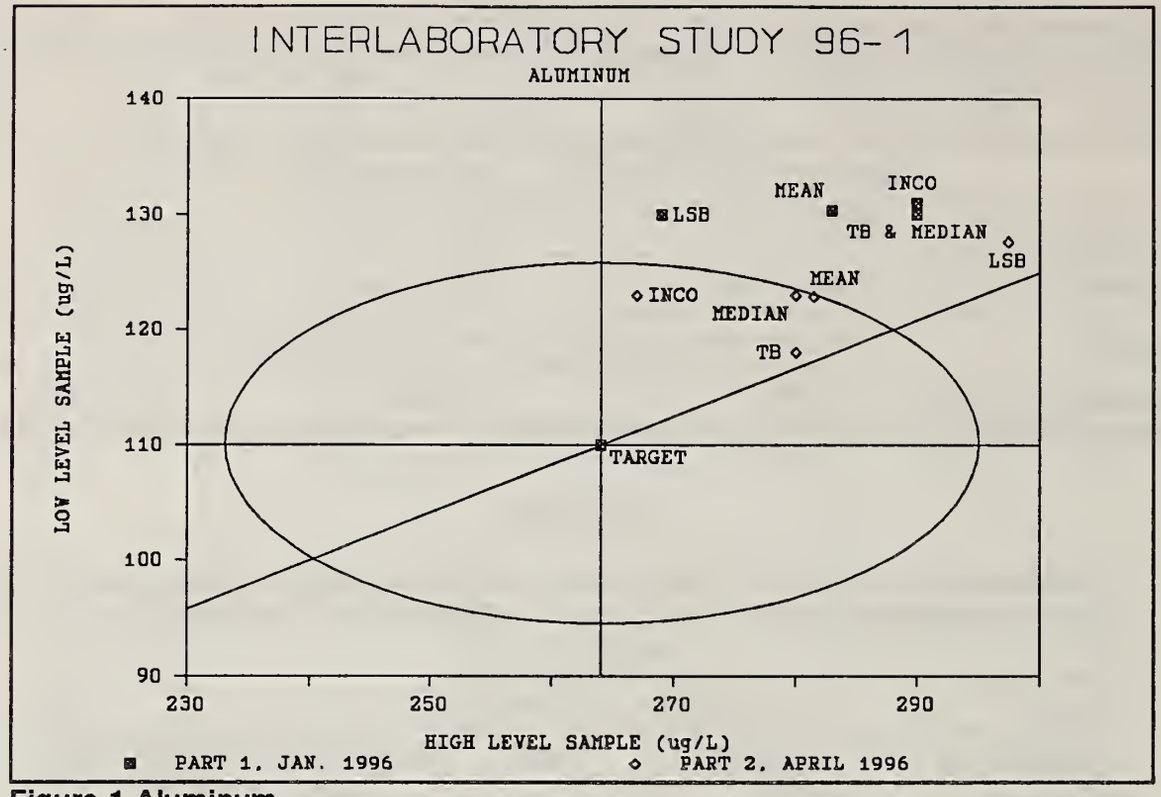

Figure 1 Aluminum

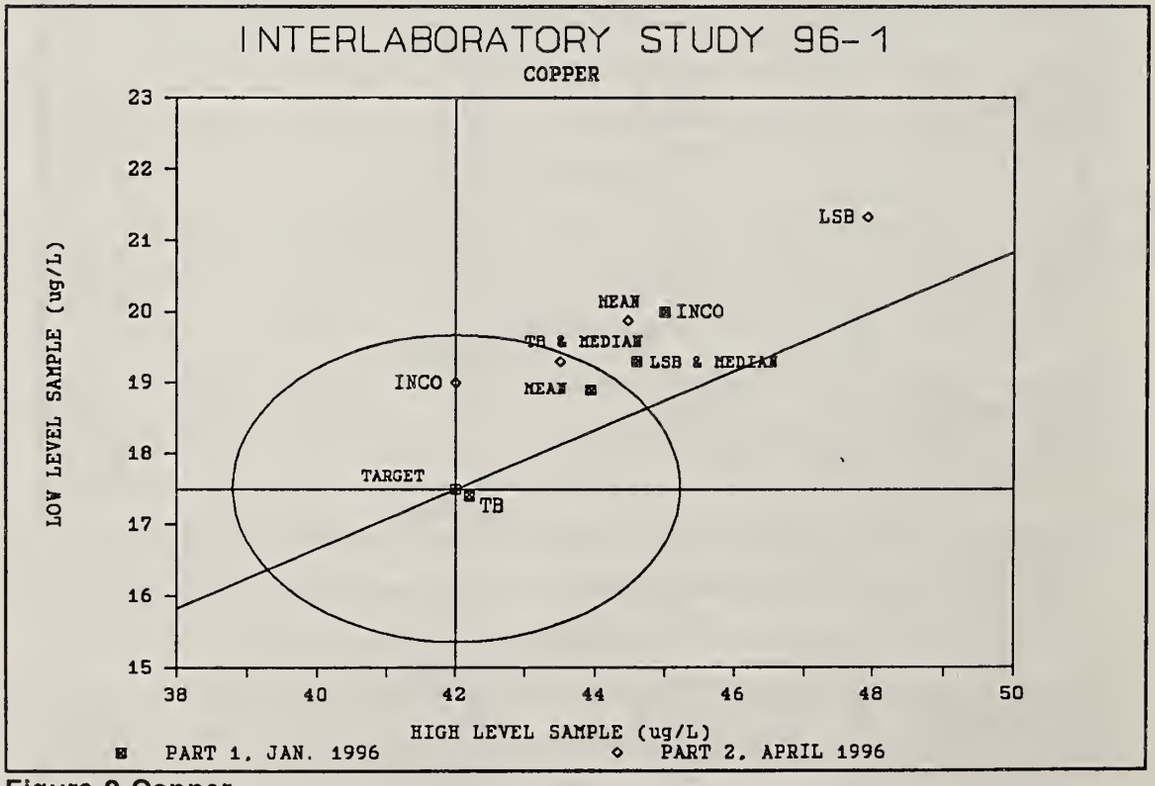

Figure 2 Copper

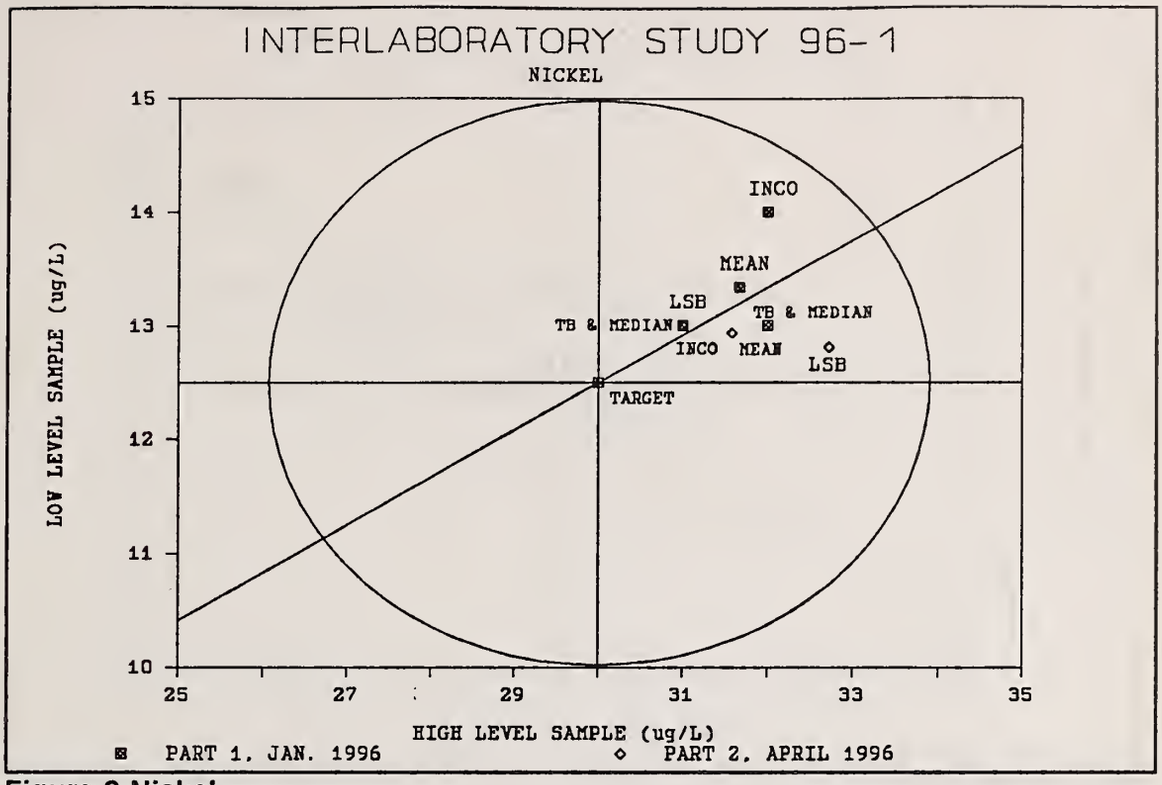

Figure 3 Nickel

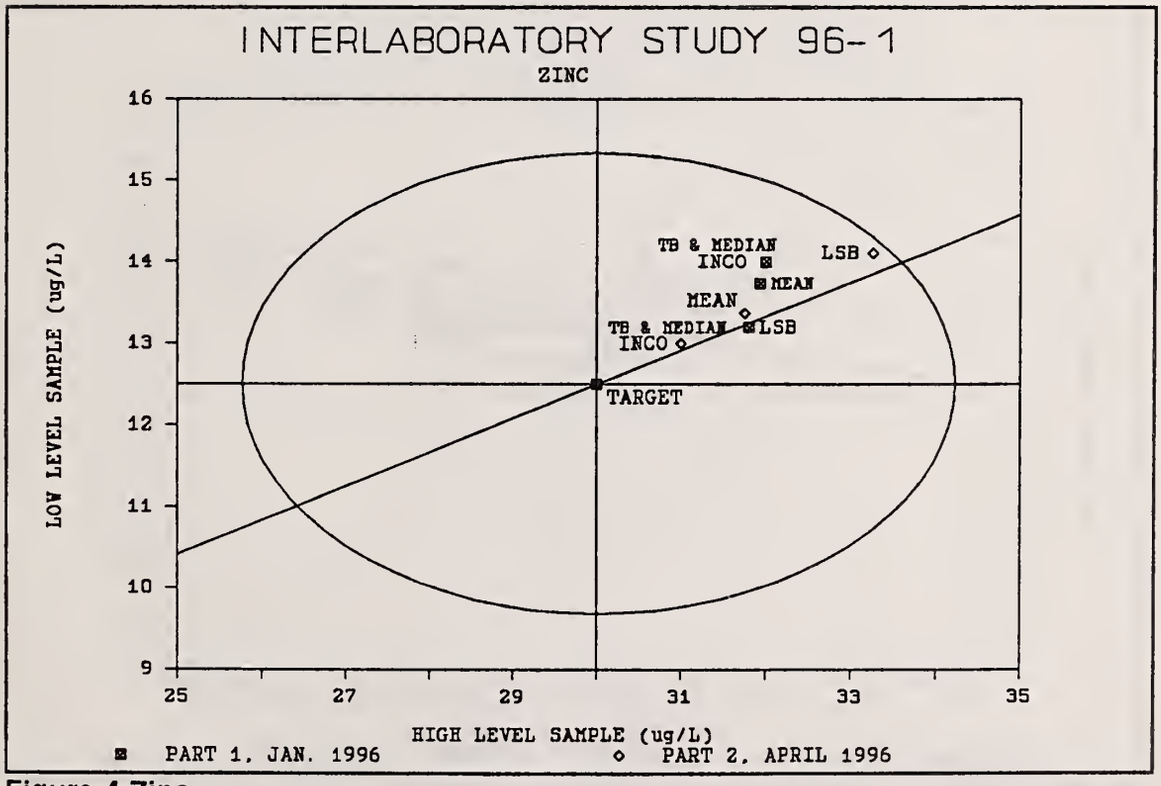

Figure 4 Zinc

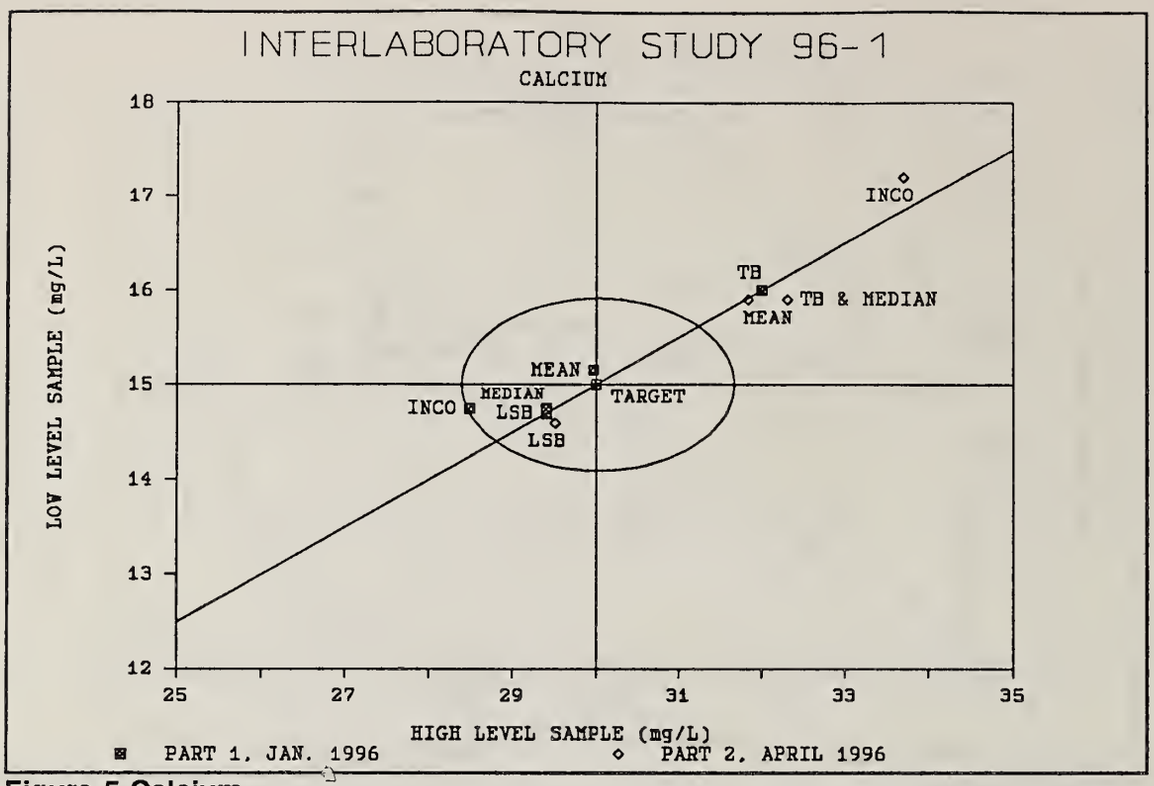

Figure 5 Calcium

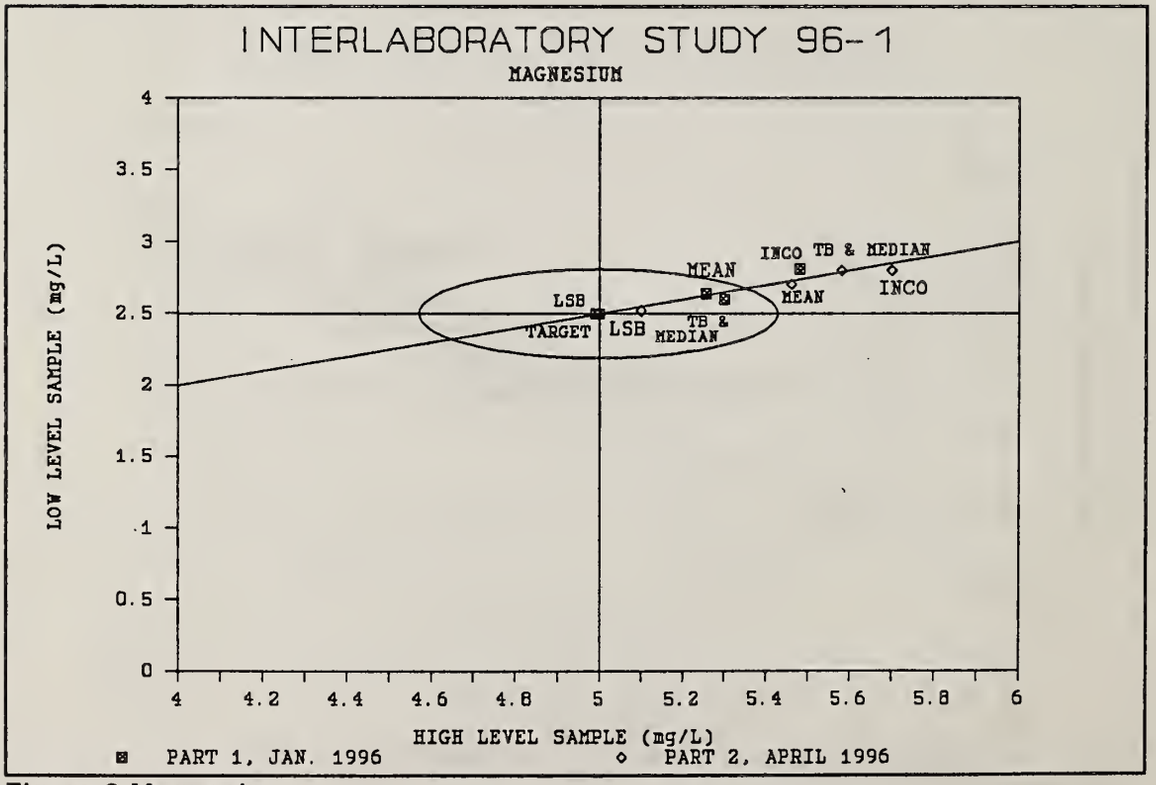

Figure 6 Magnesium

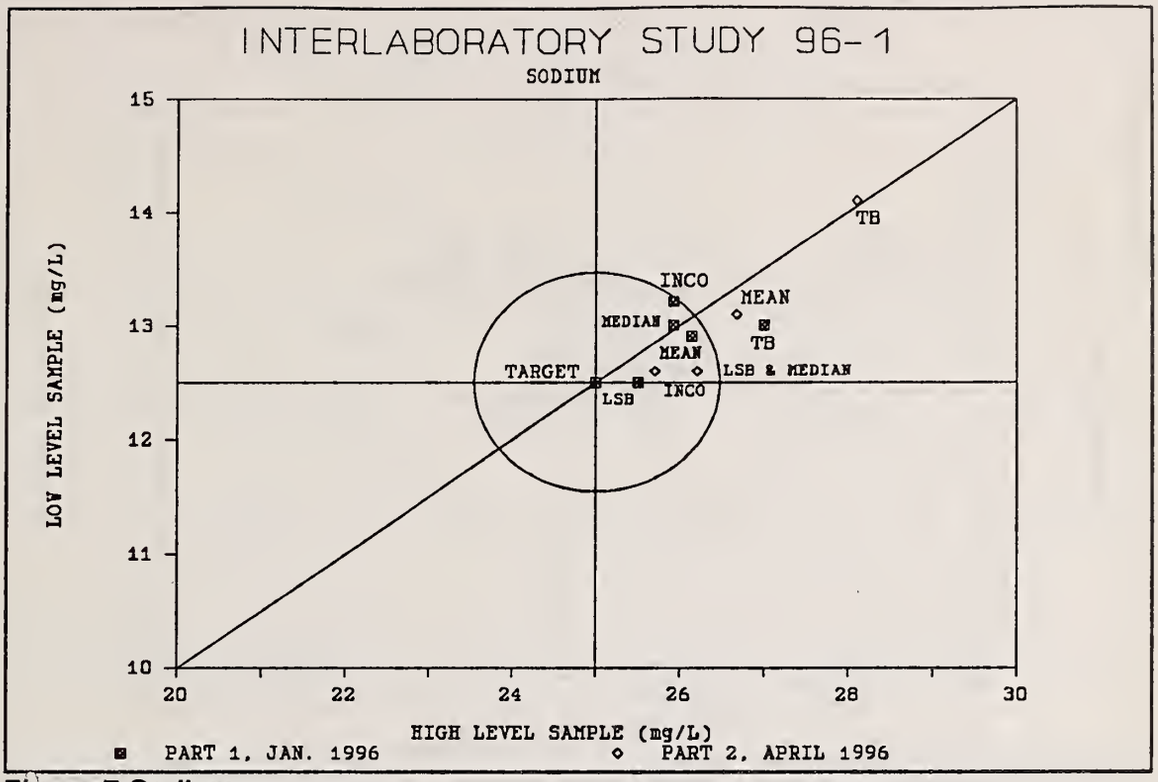

Figure 7 Sodium

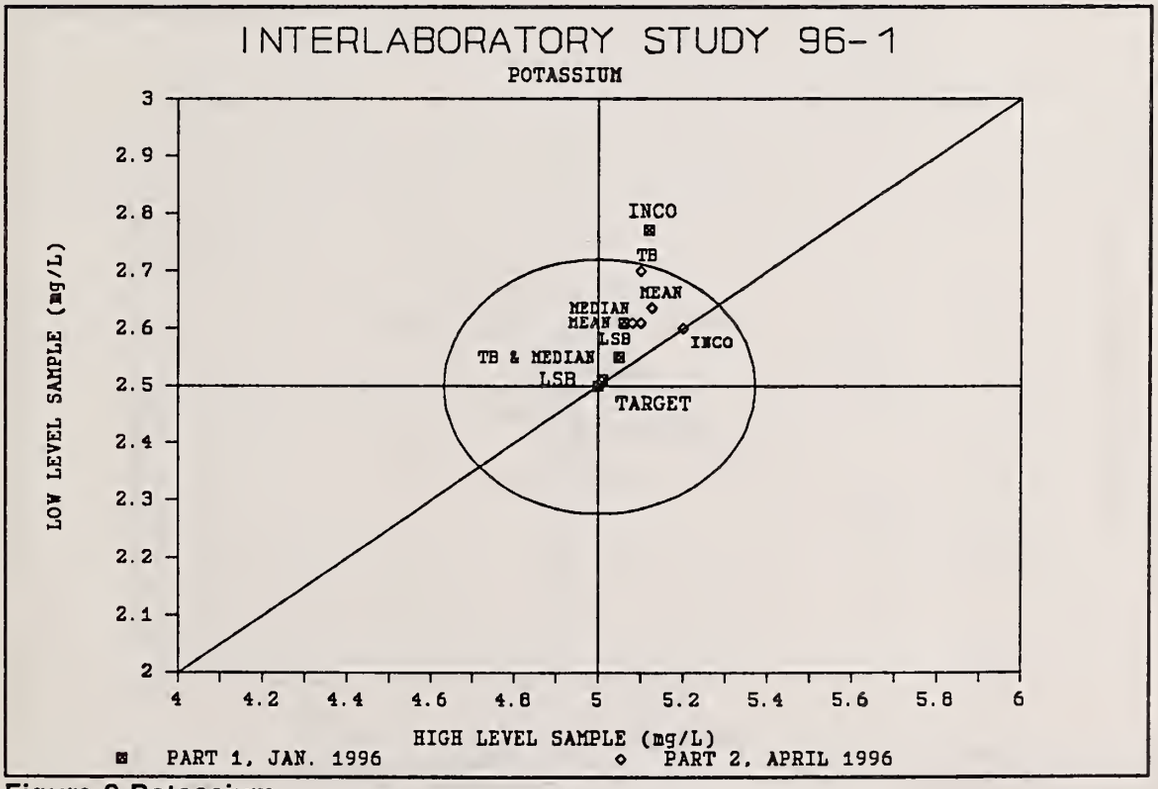

Figure 8 Potassium

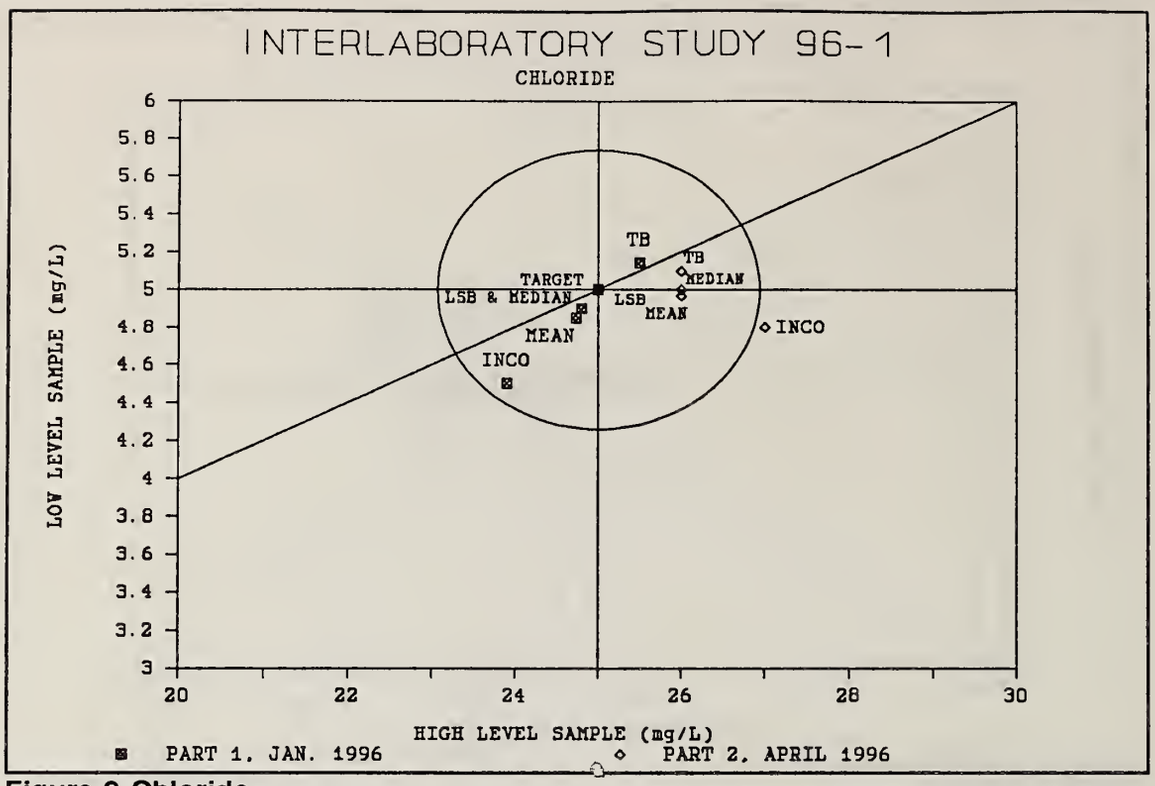

Figure 9 Chloride

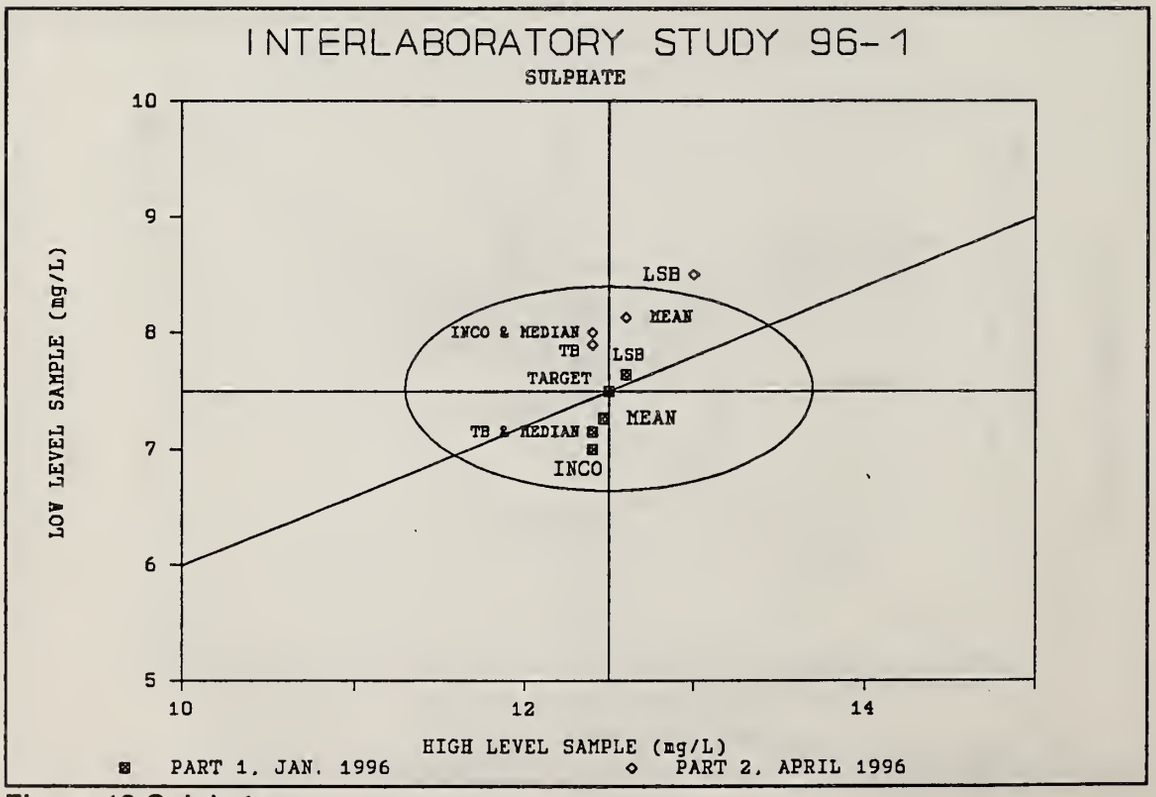

Figure 10 Sulphate

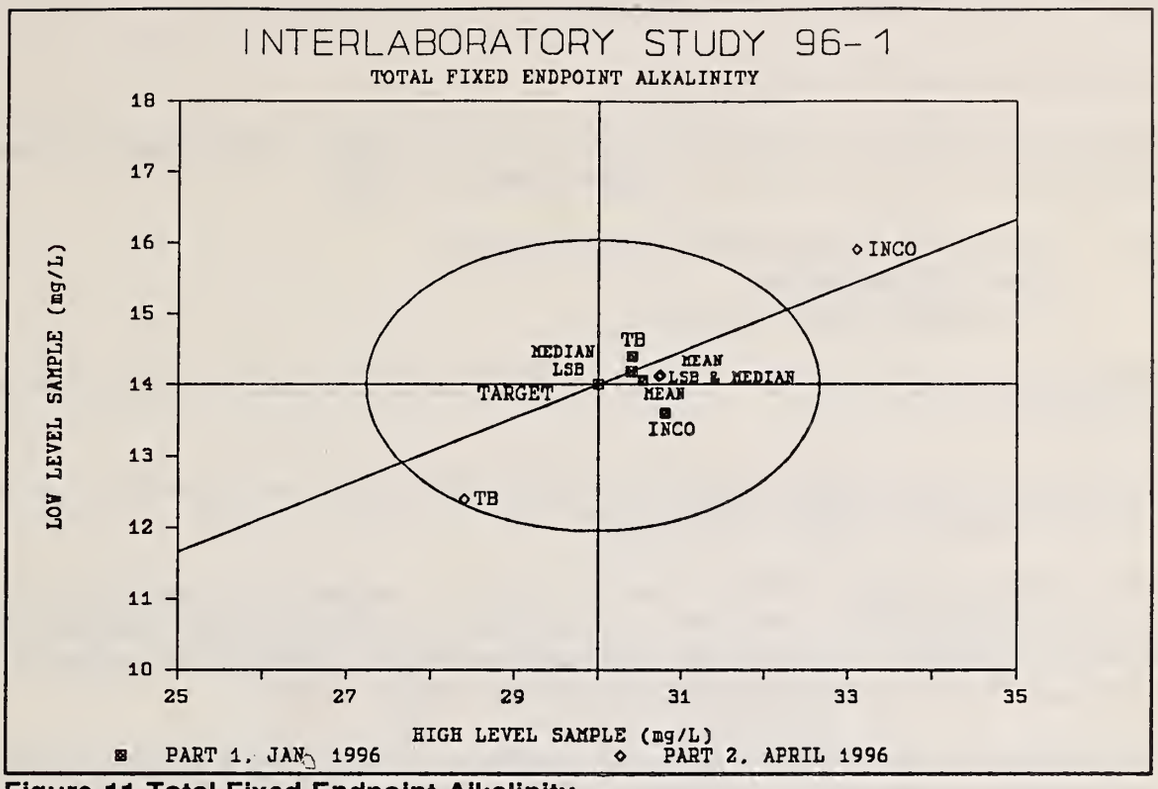

Figure 11 Total Fixed Endpoint Alkalinity

8 APPENDIX 3 - NWRI PERFORMANCE CRITERIA

The following is taken from References 2 and 3.

Three terms are used to define the acceptable difference from the target value (design or interlaboratory median) that is allowed without a result being flagged either low or high:

LLBAE: Lower Limit for Use of Basic Acceptable Error
BAE: Basic Acceptable Error
CEI: Concentration Error Increment

For a sample whose target value is at or below the LLBAE, the BAE is used to determine the range of acceptable deviations.

eg. For parameter X, the LLBAE is 10 µg/L and the BAE is 1.0 µg/L. If the target is 5.0 µg/L, then the range of acceptable results is 5.0 ± 1.0 µg/L.

For samples whose target value is greater than the LLBAE, an allowance is made for the increased variability due to concentrations. For almost all substances it appears that the variability of results increases with concentration. The allowance in added to the BAE. It is calculated by multiplying the CEI (as a percentage) by the difference between the target value and the LLBAE.

eg. For parameter Y, the target value is 21 µg/L, the BAE is 1.0, the LLBAE is 10 µg/L, and CEI is 0.1. The acceptable difference or standard criterion is calculated using the equation **(Target - LLBAE)*CEI + BAE**. In this example, the standard criterion would be (21-10)*0.10 + 1.0 = 2.1. The range of acceptable results would be 21 ± 2.1 µg/L.

In general, for the NWRI QA studies, the values chosen for the BAE and the CEI are selected so that good precision may be inferred. Historically, for the Federal-Provincial QA Program, for moderate ranges, this has be achieved with the 10% Deviation Rule.

The following table lists the standard criterion calculated for this interlaboratory study.

Parameter	LLBAE	BAE	CEI	Target (Design) Value (mg/L)	Standard Criterion
Alkalinity	1.00	1.50	0.04	14 30	2.02 2.66
Calcium	1.00	0.20	0.05	15 30	0.9 1.65
Magnesium	1.00	0.20	0.06	2.5 5	0.3 0.425
Sodium	1.00	0.50	0.04	12.5 25	0.96 1.46
Potassium	0.50	0.10	0.06	2.5 5	0.22 0.37
Chloride	1.00	0.50	0.06	5 25	0.74 1.94
Sulphate	1.00	0.50	0.06	7.5 15	0.89 1.19
Aluminum	0.0050	0.0050	0.1000	0.1100 0.2640	0.0155 0.0309
Copper	0.0015	0.0015	0.0060	0.0175 0.0420	0.00216 0.00321
Nickel	0.0015	0.0015	0.0060	0.0125 0.0300	0.00246 0.00393
Zinc	0.0020	0.0020	0.0080	0.0125 0.0300	0.00284 0.00424

QD
142
C87
MOE

Cussion, Sylvia
Total alkalinity,
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trce metals in water

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